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(11) **EP 1 344 747 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
17.09.2003 Bulletin 2003/38

(51) Int Cl.7: **C01B 15/029**, B01J 31/10,
B01J 23/42, B01J 23/44

(21) Application number: **02380057.6**

(22) Date of filing: **14.03.2002**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

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(54) **Catalyst and process to obtain hydrogen peroxide**

(57) In this invention, a process to obtain hydrogen peroxide solutions by means of the direct reaction of hydrogen and oxygen in the presence of a solvent and of catalysts constituted from noble or semi-noble metals,

or combinations of several of these metals, supported on a halogen-free acid resin, is described.

EP 1 344 747 A1

Description

FIELD OF THE INVENTION

[0001] The invention refers to a process to obtain a hydrogen peroxide solution by means of a direct reaction of hydrogen and oxygen in the presence of a solvent and of a catalyst comprising, at least, a noble or semi-noble metal supported on a halogen-free acid resin.

BACKGROUND OF THE INVENTION

[0002] Hydrogen peroxide is a highly important commercial product widely used as a whitening agent in the textile or paper industries, as a disinfectant and as a basic product of the chemical industry, e.g. in the production of peroxide compounds (sodium perborate, sodium percarbonate, metallic peroxides or percarboxylic acids) in oxidation reactions (manufacture of amine oxides), epoxidation and hydroxylation (manufacture of plasticizers and stabilizers). It is further used for cleaning surfaces in the semiconductor industry, chemical polishing of copper, tin and other copper alloy surfaces, etching electronic circuits, etc.

[0003] The industrial method currently most widely used for the production of hydrogen peroxide is the autoxidation of alkylanthrahydroquinones. This process, which is comprised of a series of phases of reduction, oxidation, extraction, purification and concentration, is very complicated which makes the investments and variable costs very high. A very attractive alternative to this process is the production of hydrogen peroxide directly from the reaction between hydrogen and oxygen in the presence of metal catalysts of the platinum group, using explosive hydrogen concentrations (United States patents US 4,681,751, US 4,772,458, US 4,832,938, US 5,338,531), outside the explosivity limit (WO 99/41190, WO 01/05498, WO 01/05501, US 6,168,775 B1). However, a high concentration of H⁺ and Br⁻ ions is necessary in this process in the reaction medium to obtain high concentrations of hydrogen peroxide. Those ions are obtained from strong acids, such as sulphuric, phosphoric, hydrochloric or nitric and inorganic bromides. Nevertheless, working with high acid concentration solutions requires the use of special equipment to avoid corrosion. Furthermore, the presence of acid solutions and halogenated ions favours the solution of active metals (platinum group) which causes, firstly, the deactivation of the catalyst and, due to the very low dissolved metals concentration, its recovery is non-viable.

[0004] To avoid these inconveniences alternative processes have been proposed without the presence of halogen ions and/or acids in the reaction medium. For example, in the European patent no. EP 492064, a palladium based catalyst supported on a resin functionalized with halogens is proposed. The reaction medium is water with a hydrogen peroxide stabilising agent, but the H₂O₂ concentrations reached were only around 0.58%

in weight. Another alternative (EP 504741), is the use of palladium catalysts supported on superacid inorganic solids, such as molybdenum, zirconium or wolfram, however, the hydrogen peroxide concentration reached did not exceed 1% in weight. In the European patent EP 978316, a process to obtain hydrogen peroxide solutions using palladium catalysts supported on active carbon functionalized with sulphonc groups is described. Nevertheless, said method requires many stages, it is very complicated to control the quality of the initial active carbons and the catalysts are difficult to reproduce.

[0005] Thus, there is the necessity to have new catalysts available which permit obtaining hydrogen peroxide by means of a direct reaction with hydrogen and oxygen in the presence of said catalysts, easily preparable and reproducible, and of a solvent, to obtain high concentration non-corrosive hydrogen peroxide solutions with high selectivity.

SUMMARY OF THE INVENTION

[0006] An objective of this invention is to provide a process to obtain hydrogen peroxide solutions by means of a direct reaction with hydrogen and oxygen in the presence of a solvent and a catalyst that comprises a supported noble or semi-noble metal, that resolves completely or partly the previously mentioned inconveniences in relation to the state of the art processes.

[0007] The inventors have observed that said objective can be achieved using a catalyst comprising, at least, a noble or semi-noble metal supported on a resin that (i) contains, at least, one functional acid group and (ii) is halogen-free. A process such as that provided for this invention permits obtaining high concentration non-corrosive hydrogen peroxide solutions with high hydrogen selectivity.

DETAILED DESCRIPTION OF THE INVENTION

[0008] This invention refers to a process to obtain a hydrogen peroxide solution by means of the direct reaction of hydrogen and oxygen in the presence of a solvent and a catalyst comprising, at least, a noble or semi-noble metal supported on an halogen-free acid resin.

[0009] The process in accordance with this invention uses catalysts comprising, at least, a noble or semi-noble metal supported on a halogen-free acid resin, unlike the process described in the patent EP 492064, which describes the use of palladium catalysts supported on resin functionalized with halogens. The inventors, surprisingly, have discovered that using catalysts comprising, at least, a noble or semi-noble metal supported on a halogen-free acid resin and using the reaction conditions described herein can obtain non-corrosive hydrogen peroxide solutions, with high concentration (e.g. equal to or above 1% in weight, preferably equal to or above 3% in weight, more preferably equal to or above 5% in weight) and high hydrogen selectivity (e.g. equal

to or above 50%) by direct reaction between hydrogen and oxygen.

[0010] The support employed in the catalysts used in the process of this invention includes a resin functionalized with halogen-free acid groups. The resins used in this invention are formed by the reaction of homopolymerization of monomers or by the copolymerization of two or more monomers. By way of an illustration, said resin includes styrenic, acrylic, metacrylic polymers, or styrene-divinylbenzene copolymers. These resins can be functionalized with different types of acid groups such as sulphonic, carboxylic, dicarboxylic, etc. (Encyclopedia of Chemical Technology Kirk-Othmer 3rd Edition, Vol. 13, p.678-705, Wiley-Interscience, John Wiley and Sons, 1981). Furthermore, the resins used in this invention may have an inorganic part, in such a manner that the resins can be deposited on the surface of an inorganic solid. These resins can be easily obtained at an industrial level. It would be convenient to indicate whether said resins are commercial products or, alternatively, to include a bibliographic reference where the possible acquirement of said resins are described.

[0011] In a specific embodiment, said halogen-free resin is a sulphonated styrene and divinylbenzene copolymer.

[0012] The catalyst is prepared by adding a noble or semi-noble metal belonging to groups VII to XI of the periodic table, preferably palladium, platinum, silver, gold, rhodium, iridium, ruthenium, osmium, or a mixture of 2 or more of these metals, to the support (non-halogenated acid resin). Amongst those preferred are palladium or a mixture of palladium with another metal, e.g. platinum. The quantity of metal supported can be between 0.001% and 10% in weight with respect to the support, preferably between 0.1% and 5% in weight with respect to the support. The addition of metal can be performed using any of the known preparation techniques of supported metal catalysts, such as, e.g. impregnation, adsorption, ionic exchange, etc. For the impregnation, one can use any kind of organic or inorganic salt of the metal to be impregnated, that is soluble in the solvent used in the addition of the metal, such as acetate, nitrate, halide or oxalate, etc.

[0013] Hydrogen peroxide formation is carried out by means of a direct reaction between hydrogen and oxygen within a solvent in the presence of a catalyst and, optionally, with the addition of an inert gas. Nitrogen, carbon dioxide, helium, argon, etc. can be used as inert gases. The working pressure is normally above atmospheric pressure, and preferably between 2 and 30 MPa. The molar relation between hydrogen and oxygen ranges from 1/1 to 1/100. The hydrogen concentration in the gas phase in contact with the reaction medium should preferably be below 4.16% molar, to maintain the operation outside the explosivity limits of the hydrogen and oxygen mixtures.

[0014] The solvents that can be used in this invention are those compounds with an inert character in the op-

eration conditions during the formation of hydrogen peroxide by direct reaction between hydrogen and oxygen. As solvents, in the framework of this invention, one can state water, C₁-C₁₂ alcohols, C₁-C₁₂ glycols or their mixtures. As regards alcohols, one can use aliphatic alcohols such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, 2-methyl-1-propanol, 1-pentanol, etc.; cycloaliphatic alcohols such as cyclohexanol, cyclooctanol, etc.; and aromatic alcohols such as 1-phenylethanol, 2-phenylethanol, etc. As regards glycols, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, etc. can be used.

[0015] The reaction of oxygen with hydrogen is performed at temperatures ranging from -10°C to 100°C, preferably from 10°C to 75°C.

[0016] The process of this invention can be carried out continuously, semi-continuously or discontinuously, by conventional techniques, e.g. in a stirred tank reactor with suspended catalyst particles, in a basket type stirred tank reactor, etc. Once the reaction has reached the desired conversion levels, the catalyst can be separated by different known procedures, such as, e.g. by filtration if the suspended catalyst is used, which would permit its subsequent reutilization. In this case, the quantity of catalyst used corresponds to that necessary to obtain a 0.01% to 10% concentration in weight with respect to the solvent and preferably between 0.1% and 5% in weight.

[0017] The reaction can be performed, likewise, in a fixed bed reactor, in accordance with known procedures. For this, the solvent and gaseous current of oxygen and hydrogen are made to circulate over the catalyst bed, in the presence of an inert gas (or not) in parallel or in counterflow in the above-mentioned temperature and pressure conditions.

[0018] The reaction to obtain hydrogen peroxide in accordance with this invention can be performed, if desired, in the presence of a promoter to improve the H₂O₂ yield. These promoters, which in general are composed of halogens, can be, e.g. bromide compounds such as hydrobromic acid, sodium bromide, potassium bromide or ammonium bromide, or chlorine compounds such as hydrochloric acid, sodium chloride, potassium chloride or ammonium chloride. The quantity of promoter used, in this case, to put this invention into practise is not critical and can range from 10⁻⁷ and 10⁻² moles per litre, preferably between 10⁻⁶ and 10⁻⁴ moles per litre.

[0019] If desired, a hydrogen peroxide stabilising agent can be added to the reaction medium. As hydrogen peroxide stabilising agents, one can quote inorganic acids such as phosphoric acid, sulphuric acid, nitric acid, etc.; organic acids such as aminomethylenephosphoric acid etc.; amino acids such as leucine, etc.; phosphoric acid salts such as sodium pyrophosphate, etc.; chelating agents such as ethylenediaminetetraacetic acid (EDTA), etc.; surfactant agents such as alkylbenzyl sulphonates, etc. These stabilisers can be used individ-

ually or in mixtures of two or more of them. The preferred stabilisers in this invention are aminomethylenephosphoric acid, 1-hydroxyethylene-1,1-diphosphoric acid, ethylenediamino-tetramethylene-phosphoric acid, the sodium salts of said compounds and sodium pyrophosphate. The stabiliser concentration depends on the type of stabiliser and hydrogen peroxide concentration. However, it is preferable to maintain the stabiliser concentration sufficiently low enough to avoid the catalyst metal from dissolving and/or the corrosion of the reactor used. In general, the quantity of stabiliser added is less than 0.5% in weight with respect to the solvent and preferably below 500 ppm.

[0020] The following examples serve to illustrate the invention and should not be considered as limits of its scope.

Examples

[0021] Examples 1 to 3 illustrate the preparation of a catalyst according to the invention, whilst Examples 4 to 8 illustrate obtaining hydrogen peroxide solutions according to the invention.

Example 1

[0022] A catalyst was prepared from a commercial resin functionalized with sulphonic groups, Lewatit K2621® (Bayer AG) (non-halogenated macroporous resin, with an exchange capacity of 1.4 eq/l, pore diameter 70 nm, porosity 0.6 ml/g and a specific surface area BET 40 m²/g). Firstly, the resin is washed three times with acetone, using equal volumes of solvent and resin. Next, a resin suspension (4 g) is prepared with 50 ml of methanol. To this suspension, a palladium (II) acetate solution (86 mg) in acetone (20 ml) is added drop by drop. The suspension is concentrated to half the solvent in a rotative evaporator under vacuum, the temperature of the bath was 45°C. The solution was filtered and the solid obtained was washed and air-dried at 110°C for 2 hours. The palladium content was of 1.34% in weight.

Example 2

[0023] A catalyst was prepared from a commercial resin functionalized with sulphonic groups Lewatit K2641® (Bayer AG) (non-halogenated macroporous resin, with an exchange capacity of 4.8 eq/l, pore diameter 70 nm, porosity 0.3 ml/g and a specific surface area BET 35 m²/g). Firstly, the resin is washed three times with acetone, using equal volumes of solvent and resin. Next, a resin suspension (4 g) is prepared with 50 ml of methanol. To this suspension, a palladium (II) acetate solution (86 mg) in acetone (20 ml) is added drop by drop. The suspension is concentrated to half of the solvent in a rotative evaporator under vacuum, the temperature of the bath was 45°C. The solution was filtered and the solid obtained was washed and air-dried at

110°C for 2 hours. The palladium content was of 1.49% in weight.

Example 3

[0024] A catalyst was prepared from a commercial resin functionalized with sulphonic groups Lewatit K2621® (Bayer AG) (non-halogenated macroporous resin, with an exchange capacity of 1.4 eq/l, pore diameter 70 nm, porosity 0.6 ml/g and a specific surface area BET 40 m²/g). Firstly, the resin is washed three times with acetone, using equal volumes of solvent and resin. Next, a resin suspension (4 g) is prepared with 50 ml methanol. To this suspension, a palladium (II) acetate solution (86 mg) and tetra-amine platinum (II) nitrate solution (12 mg) in acetone (20 ml) is added drop by drop. The suspension is concentrated to half of the solvent in a rotative evaporator under vacuum, the temperature of the bath was 45°C. The solution was filtered and the solid obtained was washed and air-dried at 110°C for 2 hours. The palladium content was of 1.37% in weight and the platinum content was of 0.15% in weight.

Example 4

[0025] 1.6 g of the catalyst from Example 1 were put inside an autoclave with 150 mg of a methanol:water mixture (96:4) and 24 ppm of HBr, and the mixture was stabilised at 40°C. The system was pressurised with a H₂O₂.N₂ (2:48:50) mixture with a flow of 2,500 mlN/min to 10 MPa(a) without stirring, and the stirring was started up (1,500 rpm) to initiate the reaction. After 2h of the reaction a hydrogen peroxide concentration of 5.3% in weight was reached. The hydrogen selectivity was of 76%.

Example 5

[0026] 0.8 g of the catalyst from Example 1 were put inside an autoclave with 150 mg of a methanol:water mixture (96:4) and 12 ppm of HBr, and the mixture was stabilised at 40°C. The system was pressurised with a H₂O₂.N₂ (2:48:50) mixture with a flow of 2,500 mlN/min to 10 MPa(a) without stirring, and the stirring was started up (1,500 rpm) to initiate the reaction. After 2h of the reaction a hydrogen peroxide concentration of 4.9% in weight was reached. The hydrogen selectivity was of 72%.

Example 6

[0027] 0.8 g of the catalyst from Example 2 were put inside an autoclave with 150 mg of a methanol:water mixture (96:4) and 12 ppm of HBr, and the mixture was stabilised at 40°C. The system was pressurised with a H₂O₂.N₂ (2:48:50) mixture with a flow of 2,500 mlN/min to 10 MPa(a) without stirring, and the stirring was started up (1,500 rpm) to initiate the reaction. After 2h of the

reaction a hydrogen peroxide concentration of 5.8% in weight was reached. The hydrogen selectivity was of 77%.

Example 7

[0028] 0.8 g of the catalyst from Example 2 were put inside an autoclave with 150 mg of a isobutanol:water mixture (96:4) and 12 ppm of HBr, and the mixture was stabilised at 40°C. The system was pressurised with a H₂:O₂ (3.6:96.4) mixture with a flow of 2,500 mlN/min to 5 MPa(a) without stirring, and the stirring was started up (1,500 rpm) to initiate the reaction. After 1h of the reaction a hydrogen peroxide concentration of 1.4% in weight was reached. The hydrogen selectivity was of 58%.

Example 8

[0029] 0.8 g of the catalyst from Example 3 were put inside an autoclave with 150 mg of a methanol:water mixture (96:4) and 6 ppm of HBr, and the mixture was stabilised at 40°C. The system was pressurised with a H₂:O₂:N₂ (2:48:50) mixture with a flow of 2,500 mlN/min to 10 MPa(a) without stirring, and the stirring was started up (1,500 rpm) to initiate the reaction. After 2h of the reaction a hydrogen peroxide concentration of 5.0% in weight was reached. The hydrogen selectivity was of 74%.

Claims

1. A process to obtain a hydrogen peroxide solution by means of a reaction of hydrogen and oxygen in the presence of a solvent and a catalyst comprising, at least, a noble or semi-noble metal supported on a halogen-free acid resin.
2. Process according to claim 1, in which said noble or semi-noble metal is selected from the group formed by palladium, platinum, silver, gold, rhodium, iridium, ruthenium, osmium and their mixtures.
3. Process according to claim 2, in which said noble or semi-noble metal is palladium or a mixture of palladium with platinum.
4. Process according to any of claims 1 to 3, in which the quantity of the noble or semi-noble metal, or their mixtures, in said catalyst ranges from 0.001% to 10% in weight with respect to the acid resin, and, preferably, from 0.1% to 5% in weight with respect to the acid resin.
5. Process according to any of claims 1 to 4, in which said acid resin is a sulphonated styrene and divinyl-

benzene copolymer.

6. Process according to any of claims 1 to 5, in which said solvent is selected from the group formed by water, C₁-C₁₂ alcohols, C₁-C₁₂ glycols, and their mixtures.
7. Process according to any of claims 1 to 6, in which the reaction temperature between hydrogen and oxygen in the presence of a solvent and catalyst ranges from -10°C to 100°C, preferably from 10°C to 75°C.
8. Process according to any of claims 1 to 7, in which the reaction between hydrogen and oxygen in the presence of a solvent and a catalyst is carried out at a pressure above atmospheric pressure, preferably between 2 and 30 MPa, optionally in the presence of an inert gas, and with a molar relation between the hydrogen and oxygen in the gas phase ranging from 1/1 to 1/100.
9. Process according to any of the previous claims, which includes the addition of a promoter for forming hydrogen peroxide and/or a hydrogen peroxide stabilising agent.



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EUROPEAN SEARCH REPORT

Application Number
EP 02 38 0057

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,X	EP 0 492 064 A (MITSUBISHI GAS CHEMICAL CO) 1 July 1992 (1992-07-01) Comparative example 5 * column 5, line 10 - line 37; example 1 * * column 1, line 37 - line 55 * -----	1-9	C01B15/029 B01J31/10 B01J23/42 B01J23/44
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C01B B01J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 September 2002	Examiner Siebel, E
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (03.02) (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 38 0057

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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17-09-2002

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82